

Photocurrent-response study for valence-band splitting and band-gap energy of photoconductive AgGaSe₂ layers

Sangyoul Lee and Kwangjoon Hong*

Department of Physics, Chosun University, Gwangju 501-759, South Korea

Photoconductive AgGaSe₂ (AGS) layers were epitaxially grown along the <112> direction onto GaAs (100) substrates using the hot wall epitaxy method. By measuring the photocurrent (PC) spectra, three peaks were observed at the temperature range 10–100 K. These peaks are caused by the band-to-band transition from the valence-band state of $\Gamma_7(A)$, $\Gamma_6(B)$, and $\Gamma_7(C)$ to the conduction-band state of Γ_6 , respectively. Thus, the crystal-field splitting and the spin-orbit splitting were estimated to be 0.251 and 0.310 eV, respectively. However, a good agreement between optical absorption and PC-peak energy was acquired. The band-gap variation as a function of temperature on AGS was well fitted by $E_g(T) = 1.950 - 8.37 \times 10^{-4}T^2/(T + 224)$. The band-gap energy of AGS obtained at 293 K was extracted out to be 1.811 eV by means of the PC experiment and optical absorption.

Key words: photocurrent, band gap, valence band splitting, hot wall epitaxy, AgGaSe₂.

Introduction

Silver gallium diselenide (AgGaSe₂, AGS), which crystallizes to the chalcopyrite structure, has received considerable attention in recent years because of its applications in photovoltaic devices [1]. Moreover, it is one of the most environmentally-friendly materials for Cd-free buffer layers because of its high absorbance in solar cells in the ultraviolet (UV)-visible range. Optical absorption and reflection experiments have been studied to determine these applications [2, 3]. Therefore, the fundamental material parameters of the band gap and its temperature dependence were extracted from these investigation. But, the photocurrent (PC) measurement, as distinct from these parameters, has been studied for the applications in photodetection and radiation measurements. It is important to investigate the conductivity change of photoconductive materials caused by incident radiation. In a PC measurement, the absorbed photons with a higher energy than the band-gap energy create electron and hole carriers. These carriers instantly flow out through the electrodes. Therefore, the PC peak obtained corresponds to the direct band-gap energy. Moreover, the electronic transitions from the levels of the valence band to the levels of the conduction band are restricted by a selection rule based on the symmetry in the Brillouin zone [4]. Consequently, the photoresponse measurement offers valuable data about the valence-band splitting and the band-gap energies toward the higher energy stages. Thereby, the band-gap energy, spin-orbit splitting and crystal-field parameters of AGS were studied through photoconductivity measurements

[5, 6]. Despite the abundance of information obtained from a PC measurement, PC studies on AGS have been limited to a few exceptions [7, 8].

In this paper, the photoconductive AGS layers were grown using the hot wall epitaxy (HWE) method. The quality of the AGS layers grown was estimated by the double crystal X-ray diffraction (DCXD) method. The temperature dependence of the band-gap energy was observed through the optical absorption spectra and PC spectroscopic measurements. The valence-band splitting for electronic transitions restricted by a selection rule is also discussed.

Experimental

Prior to the layer growth, polycrystalline AGS was formed as follows. A quartz tube was sequentially cleaned with trichlorethylene, acetone, methanol, and deionized water. The starting materials were 6N purity shot-types of Ag, Ga, and Se. After the materials were weighed in the mole fraction of each element, they were sealed in a quartz tube to maintain a vacuum atmosphere. The sealed ampoule was placed in a synthesis furnace and was continually rotated at a rate of 1 revolution per minute. In order to avoid an explosion of the ampoule due to the Se vapor pressure, the temperature of the ampoule was gradually increased to 950 °C. The temperature was then maintained for 48 hours. To grow the AGS layer, a polycrystalline AGS ingot was used as a HWE source. The AGS layers were grown on semi-insulating GaAs (100) by the HWE method using the AGS ingot as the source material. Prior to growing the AGS layers, the GaAs substrate was cleaned ultrasonically for 1 minute in successive baths of trichloroethylene, acetone, methanol and 2-propanol, and then etched for 1 minute in a solution of H₂SO₄ : H₂O₂ : H₂O (5 : 1 : 1). The substrate was degreased in organic solvents and rinsed

*Corresponding author:
Tel : +82-62-230-6637
Fax: +82-62-234-4326
E-mail: kjhong@chosun.ac.kr

with deionized water (18.2 M Ω). After the substrate was dried off, it was immediately loaded onto the substrate holder and was annealed at 580 °C for 20 minutes to remove the residual oxide on the surface of the substrate. To find the optimum growth conditions, the grown AGS layers were estimated by measuring the DCXD spectra. The growth orientation of the AGS layers was measured using X-ray diffraction (XRD). Optical absorption was used to measure the band-gap energy using an UV-VIS-NIR spectrophotometer for a range of 630 to 710 nm with the temperature varying from 10 to 293 K. Fig. 1 presents a schematic diagram of the prepared photoconductive AGS cell and the setup apparatus for the PC measurements. As shown in Fig. 1(a), to measure the PC spectra, the two Au electrodes with a coplanar geometry on the AGS layer were fabricated by an e-beam evaporator, and the ohmic contact of the electrodes was confirmed by a current-voltage measurement. After the electrodes were connected to a wire, the sample was mounted on the holder of a low-temperature cryostat (Air Product, SA-202B). The PC spectroscopic measurements were taken while the monochromatic light emitted from a halogen lamp (650 W) illuminated the sample. As shown in Fig. 1(b), the white light coming from the halogen lamp was converted to monochromatic light by passing through the monochromator (Jarrell Ash, 82-020, F0.5m). After that, the monochromatic light passed the chopper and, finally, was focused with a convex lens onto the sample. At that time, the focused beam size was $\phi = 1$ mm. The PC flowing through the sample was amplified by a lock-in amplifier and recorded in an x-y recorder. Also, the Hall effect measurement was conducted. The PC and Hall effect measurements were achieved during the temperature variation from 10 to 293 K.

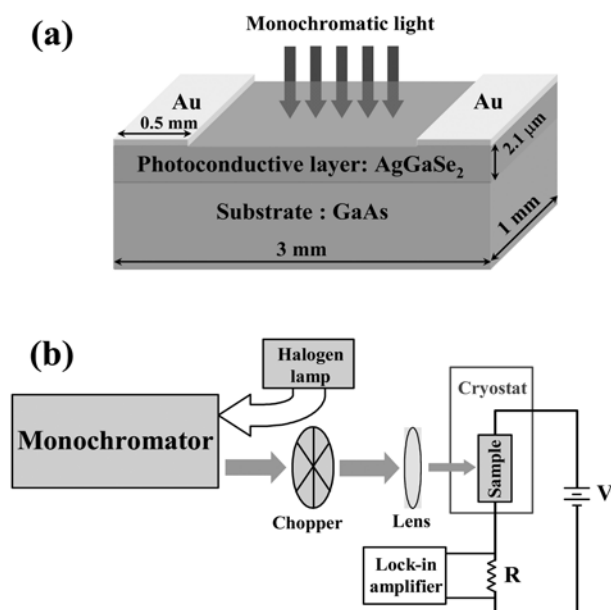


Fig. 1. Schematic diagrams of (a) the photoconductive AGS cell prepared to measure the PC spectra and (b) the setup apparatus for the PC measurements.

Results and Discussion

After the heat treatment of the substrate surface, the AGS layers grew with substrate temperatures of 400, 420, and 440 °C. At this time, the source temperature was fixed at 630 °C. The crystal quality of the grown AGS layers was evaluated from the DCXD measurements. The full width half maximum (FWHM) and intensity value of DCXD were used to evaluate the crystal quality. Fig. 2 shows the DCXD spectra of the AGS layers grown with a temperature variation of the substrate. As shown in Fig. 2, the narrowest FWHM and the strongest intensity obtained from the DCXD experiment were observed in the AGS layer grown at 420 °C. This observation indicates that the AGS layer grown at 420 °C has a very high quality. Therefore, the optimum temperature for the substrate was found to be 420 °C when the source temperature was 630 °C. The subfigure of Fig. 2 displays the XRD rocking curve to find the growth direction on the AGS layer grown at 420 °C. The rocking curve in the subfigure has three dominant peaks. These patterns correspond to the diffraction peaks of the AGS (112), GaAs (002), and GaAs (004). No other peak related to AGS beyond the AGS (112) plane was observed in the range of the XRD measurement. The observation of only one peak of the AGS (112) indicates that the AGS layer was grown along the $\langle 112 \rangle$ direction onto the GaAs (100) substrate. Furthermore, it means that the AGS layers are epitaxially crystallized even though the lattice mismatch between AGS and GaAs is very large. The results of XRD and DCXD indicate that the AGS layer of the photoconduction is a high-quality epitaxial-layer. Therefore, FWHM of DCXD on the layer grown at 420 °C was confirmed to be 215 arcsec. Also, the thickness and the growth rate of the AGS layer were 2.1 μ m and 1.9 $\text{\AA s}^{-1}$, respectively. By measuring the

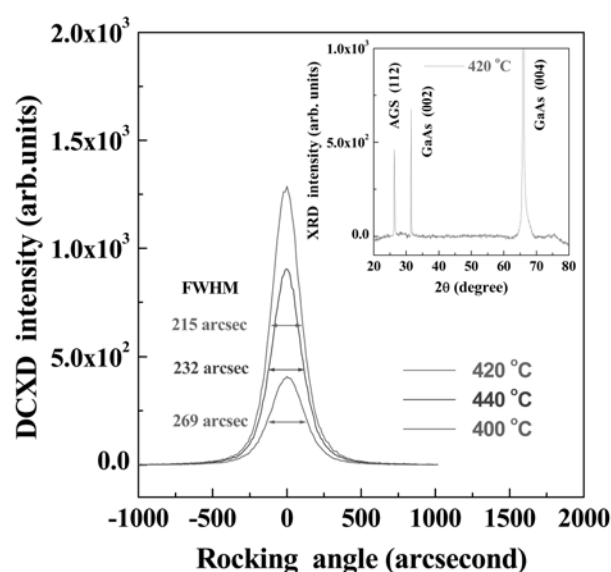


Fig. 2. DCXD spectra of the AGS layers grown with a temperature variation of the substrate (The subfigure displays the XRD rocking curve of the AGS layer grown at 420 °C).

Hall effect, the grown AGS layers were found to be n-type. The carrier density and the Hall mobility of the AGS layers were found to be $5.12 \times 10^{16} \text{ cm}^{-3}$ and $2.96 \times 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 293 K, respectively, but these values were found to be $1.12 \times 10^{15} \text{ cm}^{-3}$ and $1.01 \times 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, at 10 K, respectively.

Fig. 3 shows the PC spectra of the photoconductive AGS layers at temperatures ranging from 10 to 293 K. As shown in Fig. 3, PC spectra were observed through a wide region. Three peaks appeared in each PC spectrum below 100 K, while two peaks were observed at temperatures of 200 and 293 K. However, with a decrease in the temperature, the appearance of three peaks is related to the scattering of electrons in the valence band. It is known that the electrons in the conduction band are scattered owing to the mutual interaction between electrons when the carrier concentration of the sample is high [9]. Thus, the carrier concentration of this specimen obtained from the Hall effect measurement decreased from 5.12×10^{16} to $1.12 \times 10^{15} \text{ cm}^{-3}$ with a decrease in the temperature. When the temperature is low, the scattering probability of the carriers is lower in comparison with that at 293 K since the carriers in the valence band are in a frozen state. For this reason, three peaks could be observed in the PC spectrum below 100 K. On the other hand, two peak positions at 293 K were located at 864.6 (1.811 eV) and 601.5 nm (2.061 eV). Three peaks at 10 K were located at 636.1 (1.949 eV), 563.6 (2.200 eV), and 493.9 nm (2.510 eV). In PC measurements, the absorbed photons with an energy higher than the band-gap energy, create electron and hole carriers. If an external electric field is applied, the electrons and holes move in opposite directions. These carriers instantly flow out through the electrodes, and produce PC signals. These PC signals correspond to the direct band-gap energy. Therefore, this indicates that the PC peaks obtained are the intrinsic transition caused by the band-to-band transition [10, 11]. On the PC spectrum at 10 K, the peak at 1.949 eV, peak A, is ascribed to the electronic transition from the $\Gamma_7(\text{A})$ valence band to the Γ_6 conduction band, the peak at 2.200 eV, peak B, is

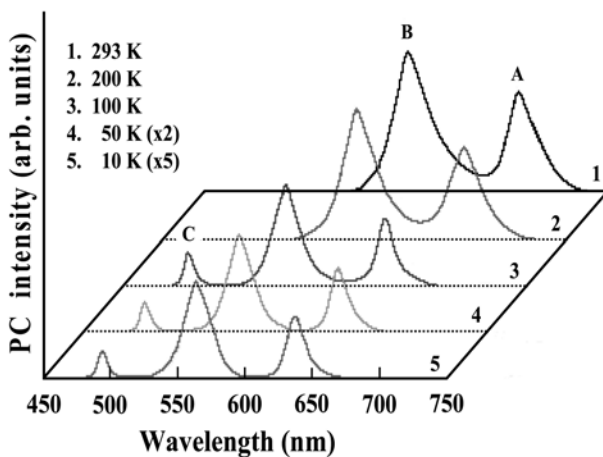


Fig. 3. PC spectra of the photoconductive AGS layers at temperatures ranging from 10 to 293 K.

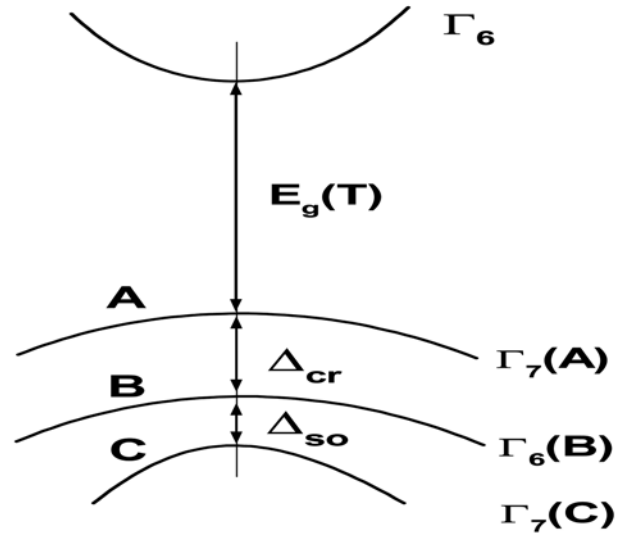


Fig. 4. Energy band structure of transitions in chalcopyrite AGS at the Γ point according to the selection rules.

associated with the electronic transition from the $\Gamma_6(\text{B})$ valence band to the Γ_6 conduction band, and the peak at 2.510 eV, peak C, is ascribed to the electronic transition from the $\Gamma_7(\text{C})$ valence band to the Γ_6 conduction band. At 293 K, the results suggested that two peaks at 1.811 and 2.061 eV correspond to the peaks A and B, respectively. Consequently, the peaks A, B, and C correspond to the band gap of AGS. Fig. 4 shows the energy band structure of transitions in chalcopyrite AGS at the Γ point according to the selection rules [1]. This figure shows that the conduction band of the s-like state has a Γ_6 symmetry, and that the valence band of the p-like state is split into three double degenerate states such as $\Gamma_7(\text{A})$, $\Gamma_6(\text{B})$, and $\Gamma_7(\text{C})$. The effective mass of the uppermost $\Gamma_7(\text{A})$ is dependent on the k-direction. The valence-band splitting was observed through the PC measurements. The crystal-field splitting, Δ_{cr} , is the energy spacing between $\Gamma_7(\text{A})$ and $\Gamma_6(\text{B})$ bands. The spin-orbit splitting, Δ_{so} , is the energy difference between $\Gamma_6(\text{B})$ and $\Gamma_7(\text{C})$ bands. Based on the above relations, the Δ_{cr} and Δ_{so} from the PC measurements were found to be 0.251 and 0.310 eV at 10 K, respectively. These values match Ref. [1]. Also, the Δ_{so} value is in excellent agreement with 0.33 eV by Bhuiyan *et al.* obtained from an absorption measurement [12]. For the chalcopyrite structure, the splitting of the valence band was generated by the deviation of the lattice constants.

Fig. 5 shows the optical absorption spectra obtained in a temperature range of 10 to 293 K. In order to identify the band-gap energy for AGS, we carefully examined the relation between the optical absorption coefficient (α) and the incident photon energy ($h\nu$) from the optical absorption measurements in Fig. 5. The relation for a direct band gap between $h\nu$ and α is as follows:

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (1)$$

where A is a function of the refractive index and hole/electron

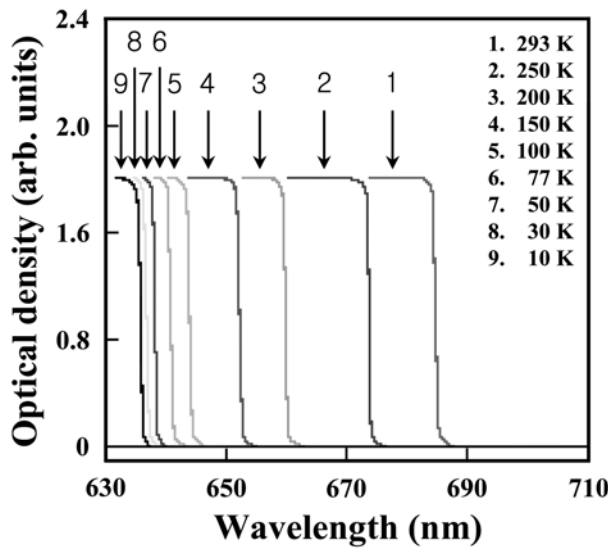


Fig. 5. Optical absorption spectra obtained in the temperature range of 10 to 293 K.

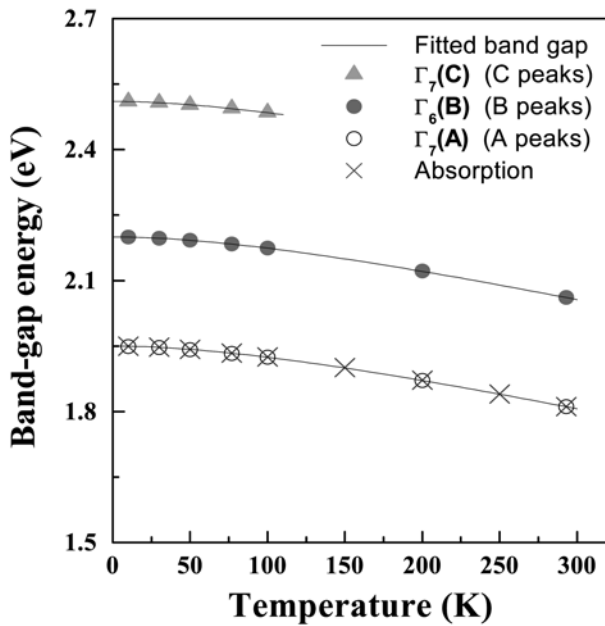


Fig. 6. Band-gap variation as a function of temperature on AGS obtained from PC and absorption measurements.

effective masses, and $h\nu$ is the energy of the incident photon. According to Eq. (1), $(\alpha h\nu)^2$ linearly depends upon the photon energy. From plots of $(\alpha h\nu)^2$ versus photon energy for different temperatures, the band gaps were determined by extrapolating the linear portions of the respective curves to $(\alpha h\nu)^2$.

Fig. 6 presents the band-gap variation as a function of temperature on AGS obtained from PC and absorption measurements. The band gaps on the AGS layer obtained from both methods were nearly equal. The PC-peak positions are consistent with the absorption calculated using Eq. (1) at the same temperature, which suggests PC measurements are a useful method for determining the band gap of the

AGS layer. On the other hand, the band-gap variation as a function of temperature can be well fitted numerically by the following formula [13]:

$$E_g(T) = E_g(0) - aT^2/(T + b), \quad (2)$$

where a is a constant and b is approximately the Debye temperature. $E_g(0)$ is the band-gap energy at 0 K. When a and b are set at 8.37×10^{-4} eV K⁻¹ and 224 K, respectively, the curve plotted in Eq. (2) closely fits the experimental values. Furthermore, the value of $E_g(0)$ is 1.950, 2.200, and 2.510 eV at the valence-band states of $\Gamma_7(A)$, $\Gamma_6(B)$, and $\Gamma_7(C)$, respectively. The Debye temperature obtained is equal to the value of 228 K reported by Ozaki *et al.* [3]. Using Eq. (2) the band-gap energy was 1.811 eV at 293 K. The direct band-gap energy for AGS ranges between 1.76 and 1.83 eV at room temperature [1, 14-16].

Conclusions

Photoconductive AGS layers were grown by the HWE method. From the results of the XRD measurements, the optimum growth-temperatures of the substrate and the source turned out to be 420 and 630 °C, respectively. Also, the AGS layer was confirmed to be an epitaxially grown layer along the $\langle 112 \rangle$ direction onto the GaAs (100) substrate. The carrier density and the Hall mobility were found to be 1.12×10^{15} cm⁻³ and 1.01×10^2 cm² V⁻¹ s⁻¹, at 10 K, respectively. From the PC measurements, three peaks in the PC spectra were observed at temperatures ranging from 10 to 100 K; however, only two peaks were observed at temperatures of 200 and 293 K. Peaks A, B, and C were associated with the intrinsic transitions caused by the band-to-band transition from the valence-band states of $\Gamma_7(A)$, $\Gamma_6(B)$, and $\Gamma_7(C)$ to the conduction-band state of Γ_6 , respectively. The Δ_{cr} and Δ_{so} of the AGS were 0.251 and 0.310 eV, respectively. The band gaps of the AGS layer obtained by PC and absorption measurements were nearly equivalent to each other. The band-gap variation as a function of temperature on AGS obeyed the equation: $E_g(T) = E_g(0) - 8.37 \times 10^{-4} T^2/(T + 224)$. Also, $E_g(0)$ was 1.950, 2.200, and 2.510 eV at the valence-band states of $\Gamma_7(A)$, $\Gamma_6(B)$, and $\Gamma_7(C)$, respectively; also the band-gap energy of AGS obtained at 293 K was 1.811 eV through the PC experiment and optical absorption.

Acknowledgement

This study was supported by the Chosun University Research Fund of 2008.

References

1. J.L. Shay and J.H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications, Pergamon, Oxford, 1975.
2. B. Tell, J.L. Shay and H.M. Kasper, Phys. Rev. B 6 (1972) 3008-3013.

3. S. Ozaki, M. Sasaki and S. Adachi, *Phys. Stat. Sol. (a)* 203 (2006) 2648-2653.
4. K.L. Greenaway and G. Harbeke, *Optical properties and band structure of semiconductors*, Pergamon, Oxford, 1968.
5. Y.S. Murty, S. Uthanna, B.S. Naidu and P.J. Reddy, *Solid State Commun.* 79 (1991) 277-283.
6. T.K. Kasumov and F.I. Mamedov, *Phys. Stat. Sol. (a)* 111 (1989) K205-211.
7. T.K. Kasumov, F.I. Mamedov and I.K. Gasuymov, *Phys. Stat. Sol. (a)* 1097 (1988) K49-55.
8. U.N. Roy, Y. Cui, R. Hawrami, A. Burger, L. Orona and J.T. Goldstein, *Solid State Commun.* 139 (2006) 527-532.
9. R.A. Smitt, *Semiconductor* (2nd Eds.), Cambridge University, Cambridge, 1978, p 72-78.
10. S.H. You, K.J. Hong, T.S. Jeong, C.J. Yoon, J.S. Park, D.C. Shin and J.D. Moon, *J. Cryst. Growth* 256 (2003) 116-121.
11. C.C. Klick, *Phys. Rev.* 89 (1953) 274-279.
12. M.R.A. Bhuiyan, M.K. Rahman and S.M. Firoz Hasan, *J. Phys. D: Appl. Phys.* 41 (2008) 235108-235113.
13. K.J. Hong, T.S. Jeong, C.J. Yoon and Y.J. Shin, *J. Cryst. Growth* 218 (2000) 19-24.
14. L. Artus and Y. Bertand, *J. Phys. C* 20 (1987) 1365-1371.
15. L.C. Tang, M.H. Lee, C.H. Yang, J.Y. Huang and C.S. Chang, *J. Phys.:Condens. Matter.* 15 (2003) 6043-6048.
16. S.N. Rashkeev and W.R.L. Lambrecht, *Phys. Rev. B* 63 (2001) 165212-165217.